MEMORANDUM

To: Tim Ratsep, SIRB

From: Rick Greene, Watershed Assessment

Re: Fraction of Inorganic Arsenic in Fish & Shellfish + Other Bioaccumulation Issues

Date: March 28, 2011

The other day during our conversation, you noted that the Burton Island RI Report (Shaw 2011) uses a value of 1.2% as the fraction of inorganic arsenic in fish and shellfish from the Inland Bays based on my research (Greene and Crecelius 2006). You asked whether use of the value was appropriate for the RI and my initial response was yes. This memo confirms that position and provides additional rationale for using the value in section 5.1 (Human Health Risk Assessment) of the RI. This memo also shares a few additional thoughts concerning terminology and methodology used in section 5.1 that I feel you should be aware of.

First, consider the 1.2% value. Not only is this value based upon Inland Bays-specific data (which should take precedence over literature values), the method used to calculate the value was conservative. Inorganic arsenic was only detected in 5 of 27 samples analyzed as a part of my study. Nondetected results were conservatively assumed to be present at one-half of the detection limit. This yielded a range of inorganic arsenic contributions from 0.7% (for summer flounder) to 1.7% (for Atlantic croaker). The average of this range is 1.2%. Most recreational anglers target multiple species and opportunistically will retain and consume whatever they catch, provided the catch meets legal requirements. Hence, use of the average among the range is appropriate in that we seek to characterize the overall picture. Coincidentally, the average among the 2 hard clam samples collected from the Inland Bays was also 1.2% (with a range of 0.97% to 1.37%). Therefore, the best estimate for a mixed diet of fish species plus clams is identical to a diet consisting exclusively of clams. This is fortuitous and suggests that a value of 1.2% is appropriate under multiple exposure scenarios.

Further support for the 1.2% number is that it's consistent with findings for fish and shellfish collected elsewhere. For example, in 117 samples collected from the American Samoa in the South Pacific, inorganic arsenic was less than 0.5% in the majority of samples, with only a few samples in the range of 1-5% (Peshut et al., 2008). Further, in 38 samples of fish and shellfish collected from Puget Sound, WA, the percent contribution of inorganic arsenic to total arsenic ranged from 0.01% to 1.8%, with an average of 0.52% and a median of 0.5% (Washington DEC 2002). Finally, only 38 out of 881 fish samples (~4%) collected nationwide between 2000 and 2003 as part of the National Study of Chemical Residues in Lake Fish Tissue actually had measurable levels of inorganic arsenic (EPA, 2009). All of these results suggest that Delaware's site-specific data is not unusual or out-of-the ordinary in any way. As an aside, the EPA appears to be embracing the growing body of evidence that inorganic arsenic is a small fraction

of total arsenic in fish. In their recent 2008 Report on the Environment (EPA, 2008), EPA used a value of 2% for assessing coastal fish.

In addition to affirming the appropriateness of the 1.2% value, I also wanted to make you aware of 1 slight terminology issue I noticed in the RI report plus 1 statement in the RI that is not entirely true. The terminology issue relates to the acronym $BAF_{sed\text{-}to\text{-}biota}$, first introduced on page 5-21. This acronym stands for sediment-to-biota bioaccumulation factor. Although the vocabulary of bioaccumulation has evolved over the years, there is now general consensus that the acronym BSAF should be used when referring to accumulation of contamination into biota from sediments, not $BAF_{sed\text{-}to\text{-}biota}$. This is a small point and may not be worth changing, especially if the EPA guidance upon which the RI relies still reflects the older acronym. On a related matter, the following statement is made on page 5-22 of the RI report: "...there are no available sediment-to-fish BAFs for the inorganic sediment COPCs." Although true in the strictest sense, this statement fails to recognize that there are sufficient sediment, fish, and hard clam data available for the Inland Bays to easily estimate BSAFs for arsenic in the Inland Bays.

A BSAF is merely the ratio of the concentration of the contaminant in the aquatic species of interest to the concentration of the contaminant in the sediments. To yield a valid BSAF, the concentration in both media should be representative of the area of interest; the data should be of similar vintage; and the data should be based on comparable analytical methods. It is my opinion that the Inland Bays data meet these criteria. Using the biota data published in Greene and Crecelius (2006), plus the EMAP/NCA sediment data (Greene 2010a and 2010b), a BSAF for summer flounder and a separate BSAF for Atlantic croaker can be readily calculated. Note that both species are demersal, with flounder often burrowing directly into sediments while croaker are found directly over bottom (Froese and Pauly, 2011). Both species feed on worms, crustaceans and other fish that reside on the bottom (Hildebrand and Schroeder, 1972). Hence, both species are strongly tied to bottom sediments for habitat and food. A BSAF is therefore a meaningful construct of contaminant transfer for these species . First consider the case of summer flounder:

$$BSAF_{flounder} = \frac{C_{flounder}}{C_{sed}} = \frac{2.1\,mg/kg}{6.5\,mg/kg} = 0.32$$

In the above equation, 2.1 mg/kg is the average concentration of total arsenic concentration among the 10 summer flounder samples reported in Greene and Creceluis (2006). The sediment concentration of 6.5 mg/kg is the average total arsenic concentration among 167 surface sediment samples collected from the Inland Bays and near-coastal waters over the period 1990 through 2006 as part of the EMAP/NCA program. Importantly, the Inland Bays-specific BSAF of 0.32 for summer flounder is nearly 3 times lower than the EPA default value of 0.9 used in the RI report. In a similar way, a BSAF of 0.11 can be calculated for Atlantic croaker, which had an average total arsenic concentration of 0.69 mg/kg. In this case, the Inland Bays-specific BSAF for croaker is approximately 8 times lower than the EPA value

used in the RI report. In both cases, a lower actual BSAF indicates that there is less transfer of arsenic from the sediments to the fish than predicted using the EPA BSAF value of 0.9. I am not suggesting that the value of 0.9 be replaced in the RI report. However, it is important for risk managers to understand that using 0.9 introduces conservatism into the analysis and means that the human health risk estimates in the RI are overstated. This would seem important since the summary of calculated carcinogenic risks for recreational fishermen (Table 5.1-11) is slightly over a *de Minimus* risk of 10^{-5}, potentially giving the impression that there's a problem.

The approach used above for flounder and croaker can also be extended to hard clam, which are well suited for a BSAF approach since they live directly in bottom sediments of the Inland Bays and we have arsenic data for the species. The average total arsenic concentration in 2 samples of hard clam from the Inland Bays is 1.23 mg/kg (Greene and Crecelius, 2006). These 2 samples actually consisted of 55 adult hard clams collected from 2 popular shellfish harvesting areas in the Bays. Again using the average sediment concentration of 6.5 mg/kg, the BSAF for hard clam becomes 0.19, which falls between that for croaker (0.11) and flounder (0.32). For hard clam, the Inland Bays-specific BSAF is approximately 5 times less than the EPA value of 0.9 that was used in the RI report. Again, this means that the EPA value, when applied to the Inland Bays, will overstate accumulation of arsenic into clams from the sediments by roughly a factor of 5. And again, this introduces conservatism into the human health risk assessment. That's fine so long as it is recognized, understood, and placed into proper context.

There is one final issue related to the BSAF and arsenic bioaccumulation that needs to be mentioned. Namely, despite all the interest and discussion concerning bioaccumulation of arsenic, actual fish and shellfish samples were not collected as part of the RI. Rather, the total arsenic concentration in fish was estimated by multiplying the EPA BSAF of 0.9 by the 95th percent UCL_{log} of the sediment arsenic concentrations near Burton Island. The inorganic arsenic concentration in the fish was then predicted by multiplying the total arsenic concentration by the expected inorganic arsenic fraction (1.2%). Importantly, both the total and inorganic arsenic concentrations predicted in the RI report following this procedure are approximately 1 to nearly 2 orders of magnitude greater than measured concentrations of arsenic in fish and shellfish from the Inland Bays. In other words, the method employed seriously overpredicts the field data. In my view, this is never good other than to say the procedure is conservative. Although the problem is acknowledged in the RI report, it is not succinctly explained. Part of the discrepancy, as explained previously, is due to a fact that the default BSAF used is 3 to 8 times greater than indicated by the field data. The remainder of the overprediction appears to be related to the use of the 95th UCL_{log} for the arsenic sediment concentration, which the RI report lists as 31.1 mg/kg. This value is considerably greater than other arsenic measurements in sediments in the Inland Bays, including those in upper Indian River (Note: EMAP/NCA results for 167 samples: ave = 6.5, median = 6.4, min = 0.125, and max = 17 mg/kg). I suspect the 31.1 value is unduly influenced by higher concentrations directly along the shoreline of the ash disposal area. I do not believe 31.1 mg/kg to be representative of the vast majority of the sediments in the Inland Bays, including the upper Indian River. Fish in the system respond to and integrate exposures over large areas of bottom, not just a narrow line along a finite length of shoreline. For this reason, I believe the arsenic concentration predicted in the

fish using the procedure in the RI is unrealistically high and unreliable. This overprediction acts to inflate calculated human cancer risk to local fishermen.

That concludes my comments on the RI. These comments supplement my earlier assessment of arsenic mass loading from the Burton Island Ash Disposal Area (Greene, 2011). Do not hesitate to contact me should you have any questions concerning this memo or the previous mass loading assessment. Thank you.

References

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